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Polarization in RMnO$_3$ multiferroics

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The review of Sim *et al.* (2016) is devoted to multiferroics RMnO$_3$ (R = Ho–Lu and Y) which possess a hexagonal crystal structure. Multiferroics are the class of crystalline materials in which at least two order parameters exist simultaneously: ferro(or anti)-ferromagnetic, ferroelectric and ferroelastic degrees of freedom. Although multierroics have been studied for 60 years (Astrov, 1960; Folen *et al.*, 1961), intensive research only started in the current century (Wang *et al.*, 2009; Khomskii, 2009; Chupis, 2011). The revival is explained by the possible application of multiferroics as magnetic sensors, capacity electromagnets, elements of magnetic memory *etc.* One of the features of multiferroic devices is the absence of thermal loss because there is no need to pass electric currents through them.

The above-mentioned review describes multiferroics with antiferromagnetic and ferroelectric orders. An interaction between these orders is realized through a crystal lattice; therefore, effects such as phonons, magnons and spin-phonon coupling can exist. These effects together with the description of crystal and magnetic structures of hexagonal RMnO$_3$ multiferroics, are presented in the review. Hexagonal multiferroics are related to the group of improper ferroelectrics. If a material is non-ferroelectric, it is characterized by a single energy potential in terms of polarization, having its minimum at zero polarization. Proper ferroelectrics are defined by a double-well potential and minimum energy at non-zero polarization. In proper multiferroics a relative displacement of the metallic sublattice in regard to the oxygen sublattice results in a spontaneous polarization, which is the primary order parameter in the ferroelectric transition. Improper ferroelectrics are characterized by single-well energy potential. The ferroelectric transition is driven by an unstable non-polar mode, which is linearly coupled with the polar mode, decreasing the energy of the latter and inducing a non-zero polarization. In improper ferroelectrics, the spontaneous polarization is a second-order parameter coupled to a primary non-polar lattice distortion.

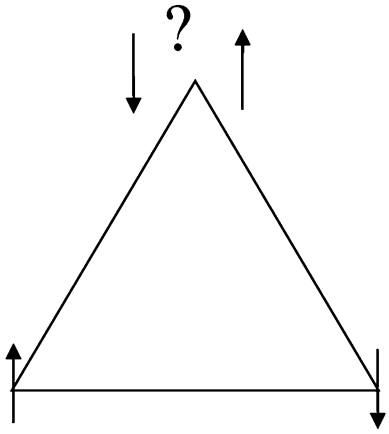
In both groups of multiferroics the coupling between the electric polarization and a magnetic field or between the magnetization and an electric field is called a magnetoelectric effect. This effect can be observed in the appearance of the electric polarization as proportional to a magnetic field and *vice versa* arising of the magnetization proportional to the electric field. The necessary condition for the existence of a linear magnetoelectric effect in a material is a violation of space and time parities separately, and a conservation of the combined space-time parity. As an example, the value of the magnetoelectric effect in YMnO$_3$ is $\sim 5.5\ \mu C\ cm^{-2}$. The much larger values of this coefficient (by two or three orders) are achieved in composite materials, in which magnetostrictive and piezoelectric layers alternate.

Experimentally the polarization is determined by measuring the electric current going through a ferroelectric capacitor when the polarization is switched. The magnitude of spontaneous polarization can also be estimated by means of calculations which apply Born effective charges Z^* and distortions τ from a centrosymmetric structure to the ferroelectric phase

$$P = \frac{1}{\Omega}\Sigma Z^*\tau,$$

where Ω is the unit-cell volume. The polarization can also be more accurately obtained using a Berry phase approximation (Resta, 1994).

Using group theoretical analysis it was found (Fennie & Rabe, 2005) that the zone-boundary K$_3$ mode and a polar zone-center Γ_2^- mode are the dominant modes in the ferroelectric distortion that relates the high-temperature paraelectric phase $P6_3/mmc$ and



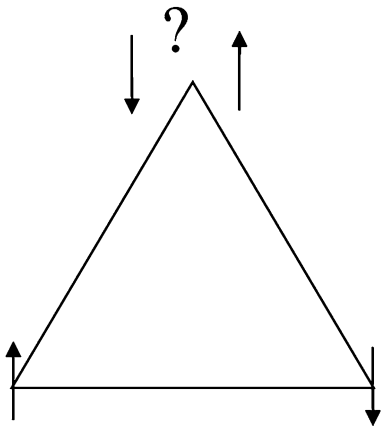


Figure 1
Illustration of frustration in a simple triangular lattice.

the low-temperature ferroelectric phase $P6_3cm$ of $YMnO_3$. The hexagonal lattice of $RMnO_3$ multiferroics belongs to geometrically frustrated structures. Fig. 1 illustrates frustration on a simple example of a triangular lattice. How should the spin in the upper vertex of the triangle be oriented such that it is antiferromagnetically ordered with respect to the other two spins?

In the review by Sim *et al.* (2016) the physical properties of only bulk multiferroics are described. Recently the first experiments were carried out on nanocrystalline materials and films of $YMnO_3$ (Bergum *et al.*, 2011). Results of these experiments show that the *c* lattice parameter increases with film thickness.

It is worthwhile mentioning materials that are not multiferroics but exhibit similar properties. For example, in the system $BaTiO_3$/Fe magnetic order extends in segnetoelectric $BaTiO_3$ across nanometer distances (Valencia *et al.*, 2011). Another example of materials which can show similar properties to multiferroics is topological isolators (Kopaev *et al.*, 2011). A band-gap forms and a strong magnetoelectric effect arises if a topological isolator covered by magnetic film is located in the magnetic field.

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